

Claims:

1. A process of producing polytrimethylene terephthalate (PTT) with an intrinsic viscosity of at least 0.75 dl/g by esterification of terephthalic acid (TPA) with tri-methylene glycol (TMG) in the presence of a catalytic titanium compound to obtain an esterification product, precondensation of the esterification product to obtain a precondensation product and polycondensation of the precondensation product to obtain PTT, characterized in that
- a) the esterification is performed in at least two stages, a first, initial stage and at least one second, subsequent stage connected to a process column,
- b) a liquid catalyst feed is prepared on base of TMG having a concentration of less than 5 wt-% titanium in the form of a titanium compound stabilized by a bifunctional organic acid,
- c) a major quantity between 65 and 100% of said liquid catalyst feed containing 35 to 110 ppm titanium, is introduced into the at least one subsequent esterification stage, operated at a temperature of 245 to 260°C, and a pressure of 0.7 to 1.2 bar,
- d) a minor quantity of said liquid catalyst feed containing 0 to 40 ppm titanium and equal in maximum to 35% of the total catalyst is directly fed to the initial esterification stage usually together with the raw materials, which direct catalyst feed can be partially or completely substituted by the same quantity of catalyst in a reaction product, which may be recycled from any further reaction stages and which is mixed to the raw materials for further reaction in said initial esterification stage in connection with a total molar TMG to TPA feed ratio of 1.15

to 2.5, a temperature of 240 to 270 °C and a pressure of 1 - 3.5 bar,

5 e) the precondensation is performed at a temperature of 245 to 260°C under a reduced pressure between 2 and 200 mbar,

10 f) the polycondensation is carried out in the melt phase at a pressure of 0.2 to 2.5 mbar, a temperature of 252 to 267°C, basically increasing from the entry to the exit of the polycondensation reactor during agitation and formation of steadily renewed, large film surfaces of the reaction product for evaporation of the split products, and

15 g) for generating the vacuum to perform the precondensation and polycondensation vapor-jet pumps are used to remove the released TMG and PTT oligomers and low boilers from the gas phase of the reactors, and the vapor-jet pumps are operated with TMG vapor, and the vapors
20 sucked off and compressed by the vapor-jet pumps and said TMG vapors are condensed by spraying them with a liquid which predominantly consists of TMG.

25 2. A process as claimed in claim 1, characterized in that said titanium compound is a titanium alkylate, like titanium tetrabutylate, titanium tetraisopropylate or tetra-(2-ethylhexyl)-titanate, or a titanium dioxide - silicon dioxide - co-precipitate or a hydrated sodium containing titanium dioxide or a titanium salt of organic
30 acids or a titanium complex with hydroxycarboxylic acids.

a 3. A process as claimed in ^{claim 1} ~~any of claims 1 to 2~~, characterized in that said liquid catalyst feed contains tri-methylene glycol, in which a C₄ to C₁₂ dicarboxylic acid is
35 dissolved below its saturation concentration.

4. The process as claimed in claim 3, characterized in that terephthalic acid or isophthalic acid is used as C₄ to C₁₂ dicarboxylic acid.

a 5 5. The process as claimed in ^{Claim 1} ~~any of claims 1 to 2~~ characterized in that said liquid catalyst feed contains tri-methyleneglycol, in which a C₂ to C₁₂ monocarboxylic acid is dissolved below its saturation concentration.

a 10 6. A process as claimed in ^{Claim 1} ~~any of claims 1 to 5~~, characterized in that the process is a continuous process.

15 7. A process as claimed in claim 6, characterized in that a part of the reaction product is withdrawn at any point between the exit of the subsequent stage of esterification and the entry to the polycondensation and mixed to the raw materials by recycling said reaction product to the first, initial esterification stage.

20 8. A process as claimed in claim 7, characterized in that said reaction product recycled to the initial esterification stage lies in the range of 5 to 40 wt-% of the nominal throughput.

25 9. A process as claimed in ^{Claim 1} ~~any of claims 1 to 5~~, characterized in that the process is a discontinuous process, and the initial process cycle with a transiently heterogeneous reaction mixture and a limited TPA-conversion of below 95% represents said 'initial stage' and the later
30 reaction cycle in a homogeneous melt phase with a TPA conversion of at least 97% represents said 'subsequent stage' of the esterification process, to which the major part of the catalyst is fed, and a portion of the reaction product kept back at the end of the precondensation is used
35 for the next discontinuous process in step d as catalyst containing reaction product.

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Claim 1

a 10. A process as claimed in ~~any of claims 1 to 9~~ characterized in that the second portion of the catalyst is fed after the esterification step.

5 11. A Process as claimed in claim 9, characterized in that said catalyst containing reaction product recycled to the initial esterification stage lies in a range of 25 to 85 wt-% of the nominal batch size.

Claim 1

10 12. A process as claimed in ~~any of claims 1 to 11~~, characterized in that the first, initial stage of esterification is conducted to a degree of esterification of 90 to 95%, and the subsequent stage of esterification is conducted to a degree of esterification of 97 to 99%.

Claim 1

15 a 13. A process as claimed in ~~any of claims 1 to 12~~, characterized in that the condensed vapors from step g are recirculated to the initial and possibly further subsequent stages of the esterification, optionally after removing of
20 the low boilers from TMG by distillation.

Claim 1

a 14. A process as claimed in ~~any of claims 1 to 13~~, characterized in that the PTT contains up to 20 wt-% comonomer units derived from other dicarboxylic acids
25 and/or diols.

Claim 1

a 15. A process as claimed in ~~any of claims 1 to 14~~, characterized in that at any point before the end of the
30 polycondensation in the melt phase usual additives ^{comprising} ~~such as~~ delustering agents and/or color agents and/or branching agents and/or stabilizers are added.

Claim 1

a 16. A Process as claimed in ~~any of claims 1 to 15~~, characterized in that said polycondensation reactor is a
35 discing reactor or a cage type reactor.

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Claim 1

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17. A process as claimed in ~~any of claims 1 to 16~~, characterized in that the PTT is after the polycondensation in the melt phase granulated to chips, and the chips are dried, crystallized and treated thermally in the solid phase.

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Claim 1

b

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18. A process as claimed in ~~any of claims 1 to 17~~, characterized in that the PTT is processed ~~to products~~^{into}, ~~like~~ fibers or filaments or films or molded articles or chips.

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19. A process as claimed in claims 18, characterized in that the processed products have an IV of 0.8 to 1.1 dl/g, a filterability of $< 40 \text{ bar} \cdot \text{cm}^2/\text{kg}$ and a thermal stability (as defined before) of $> 80\%$.